Determination of Bio-Kinetic Coefficients by Respirometry for use in the Water9 Air Emissions Model

Richard A. DiMenna

Lawrence R. Sandeen

Rohm and Haas Co.

WEF 10th Annual Industrial Waste Technical and Regulatory Conference

August 22-25, 2004

Philadelphia, PA

Rohm and Haas Bristol Plant and WWTP

- Plant produces polymer products in 4 productions area
  - Wastewater contains various acrylic monomers, styrene, solvents, surfactants
- Neutralization → Equalization → Activated Sludge Treatment
- 1.0- 1.5 MGD flow
- All tanks through aeration tanks are covered

Air Emissions from WWTP

- Plant air permit requires reporting of monthly VOC emissions from WWTP tanks
  - Emissions had been estimated using historical correlations
  - Water9 model of WWTP developed to improve technical basis for the estimates

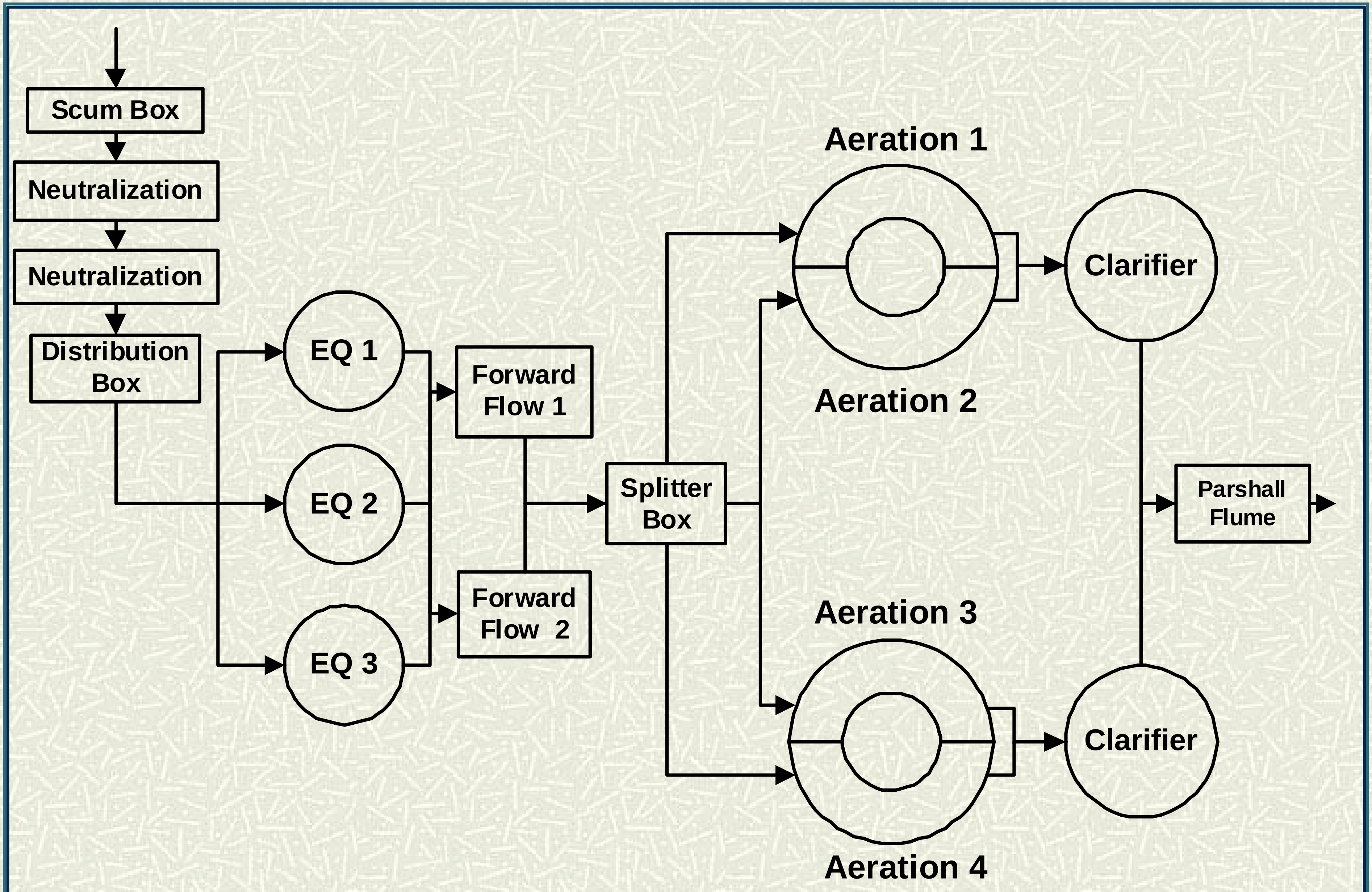
Water9 Model

- Replaces earlier Water8, Chem9 and Chemdat8 models.
- Available from US EPA at http://www.epa.gov/ttn/chief/software/water/index.html
- MS Windows interface
- Version 2.0 available April 2004, with interface, reporting and modeling improvements

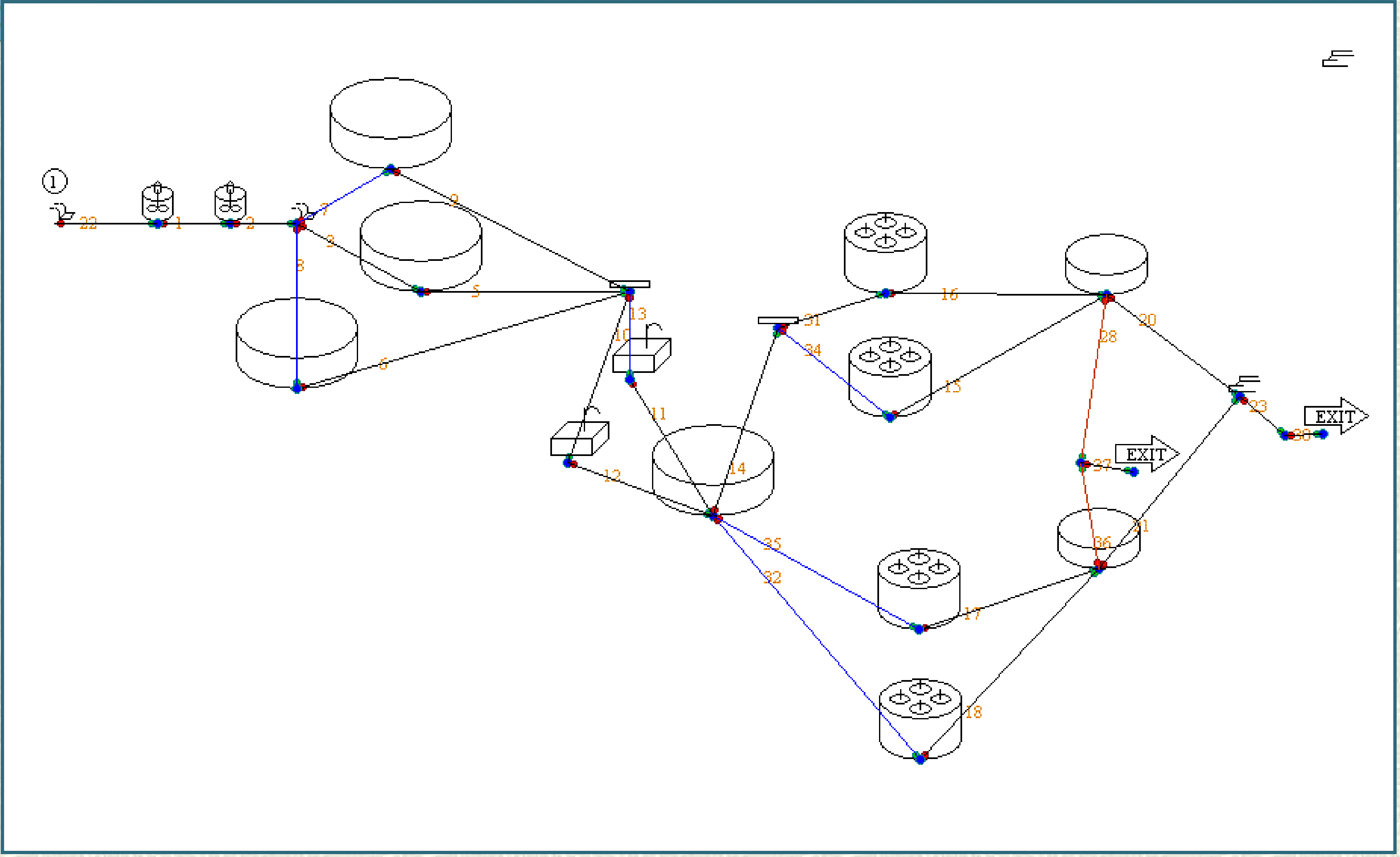
Water9 Model

- Contains modules for ~50 wastewater treatment and conveyance units
- Performs mass balance and mass transfer calculations to estimate fraction of each compound emitted to air, biodegraded and adsorbed onto solids in each unit
- Extensive database of physical properties and biodegradation kinetic constants for organic compounds, with estimation by molecular structure when no data available

Bristol WWTP



Water9 Flowsheet of Bristol WWTP



Water9 Units Used

- Mix Tank
- Weir,Waterfall
- Equalization
- Covered Separator
- Diffused Air Biotreatment
- Circular Clarifier
- Open trench

Chemicals for Water9 Modeling of WWTP

1-Butanol	Ethyl Acrylate
Methyl Ethyl Ketone	Ethylbenzene
tert-Butanol	2-Ethylhexylacrylate
Acetaldehyde	Formaldehyde
Acrylic Acid	Methacrylic Acid
Acrylonitrile	Methanol
Benzene	Methyl Acrylate
Butyl Acrylate	Methyl Methacrylate
Butyl Methacrylate	Toluene
Chloroform	Xylene
Styrene	

Preliminary Modeling Results

- Styrene air emissions, primarily from the aeration tanks, were predicted to be ~ 0.2 g/s, and effluent concentration >1 ppm_w
- All other compounds had < 0.002 g/s air emissions, including some with similar mass loadings
- Styrene effluent concentrations measured in plant effluent were typically non-detectable at < 5 ppb_w, and no noticeable styrene odor in aeration tank vents.

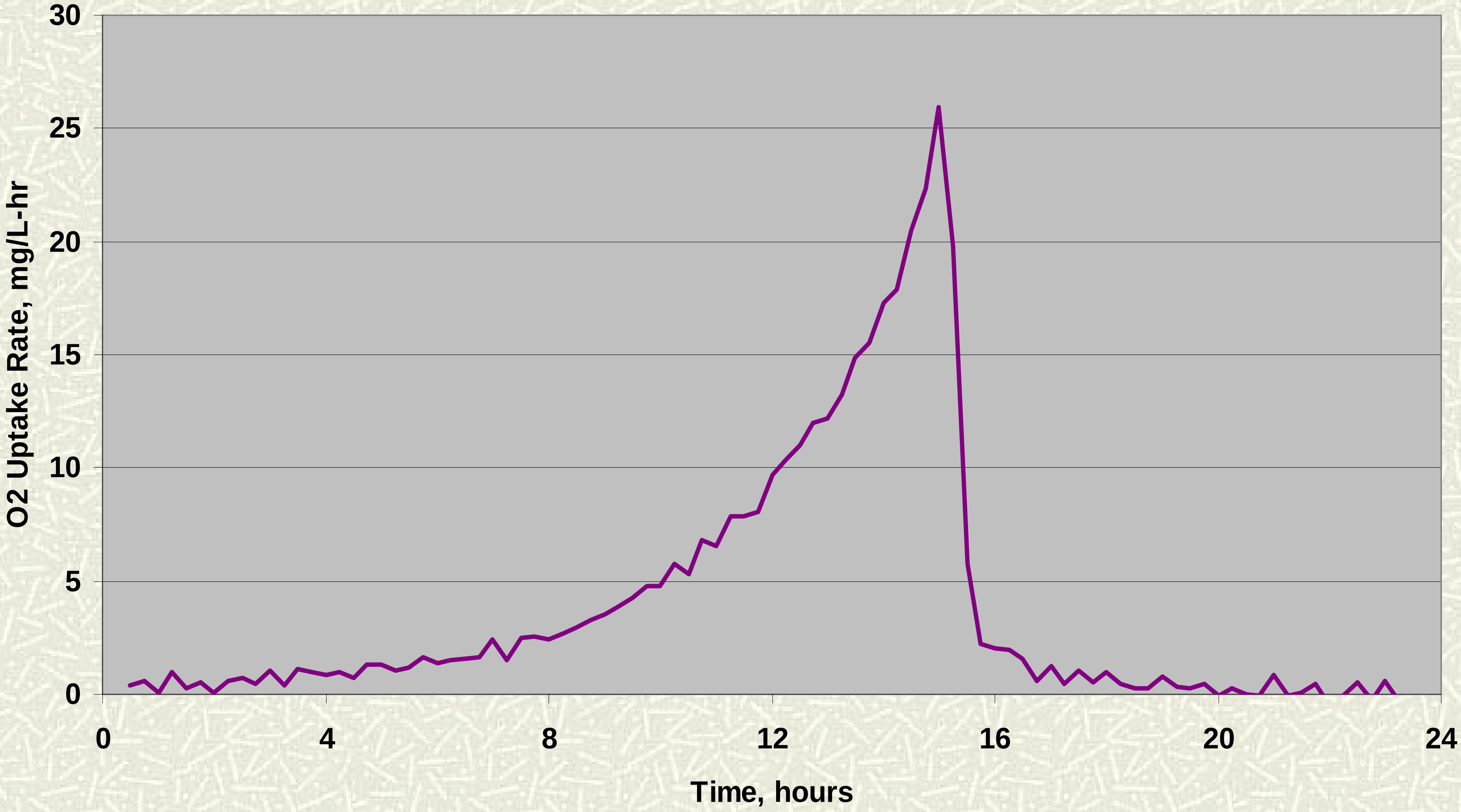
Styrene Physical Properties Review

- Comparison of Water9 default styrene physical property data to literature values indicated some minor variations, including for Henry's Law Constants and octanol-water partition coefficients
  - Alternate values of HLCs had minor effect on modeling results
  - Alternate values of other parameters had no effect

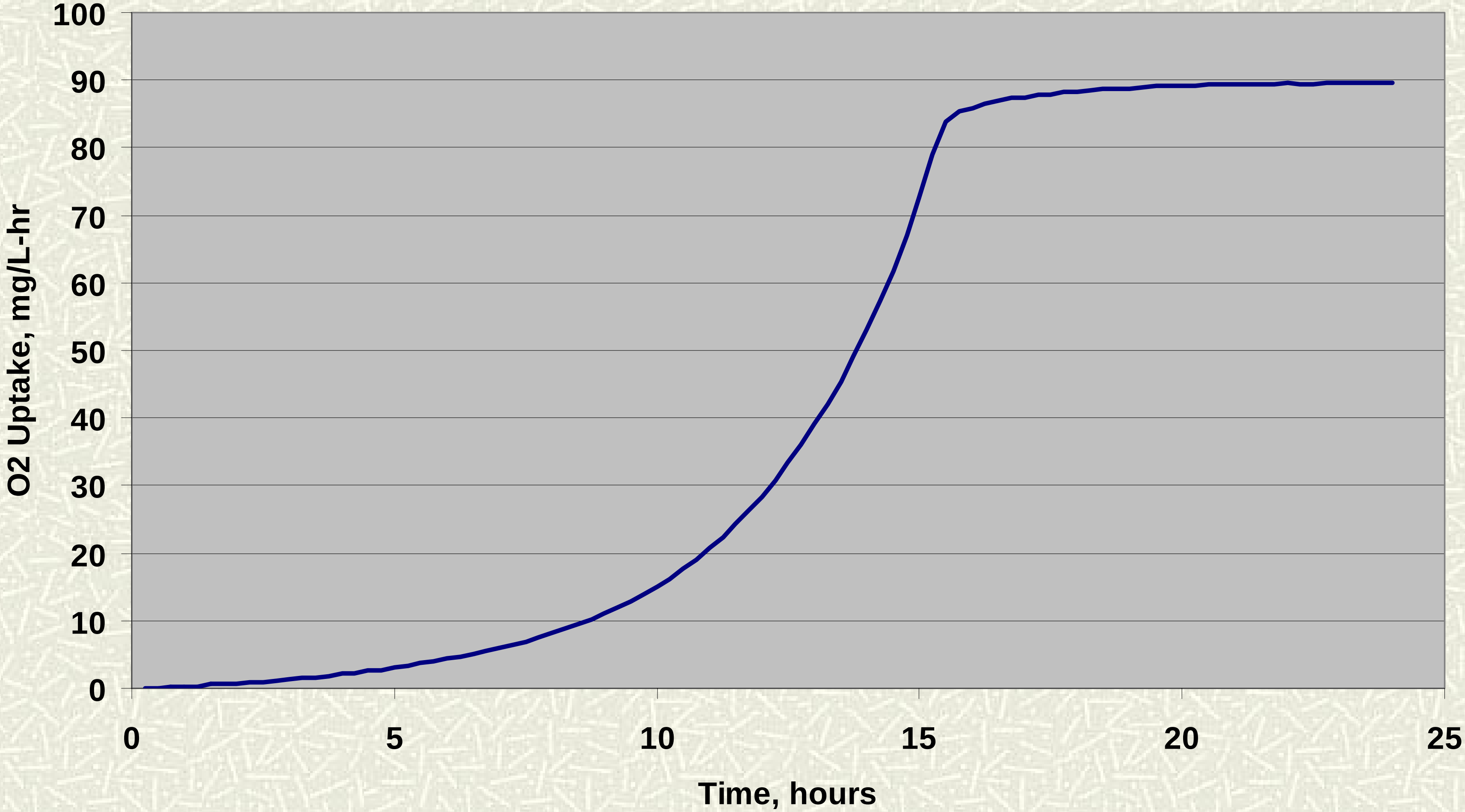
Styrene Biodegradation Kinetics

- Concluded that the default styrene bio-kinetic constants were underestimating the amount of biodegradation occurring in a system acclimated to styrene
- Laboratory respirometry unit from Challenge Environmental used to evaluate biodegradation of styrene using plant biomass

O_2 Uptake Rate from Respirometry



O_2 Uptake Data from Respirometry



Fit Respirometry Data to Monod Model

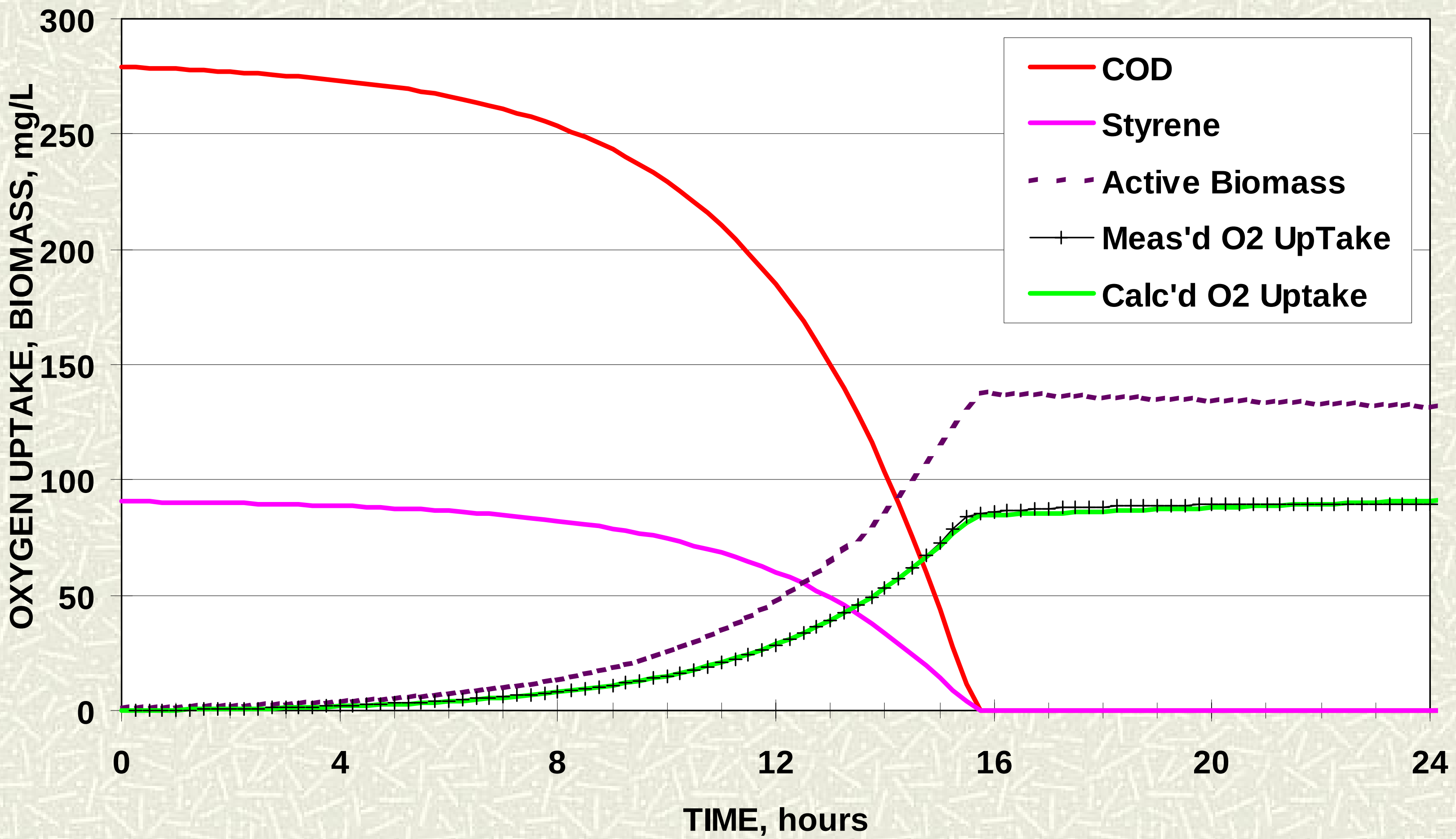
$$\mu = \frac{\mu_{max} S}{K_s + S} \quad \text{or} \quad q = \frac{q_{max} S}{K_s + S}$$

where

- μ = growth rate, hr^{-1}
- q = substrate removal rate, hr^{-1}
- K_s = half saturation coefficient, mg/L
- S = Substrate concentration, mg/L

- Best fit of O_2 uptake based on adjustments to cell yield coefficient, maximum cell growth rate (μ_{max}), K_s, decay rate, initial biomass concentration

Substrate Removal, O2 Uptake and Biomass Growth



EPA-Recommended Procedures for Determining Kinetic Constants for Water9

- Contained in 40 CFR Part 63 Appendix C and *Federal Register* of January 17, 1997
- Procedures for laboratory continuous and batch reactors, including batch serum bottle methodology.
- Procedure relate substrate reduction to total biomass.

Respirometry Kinetics vs Water9

- Respirometry Monod kinetics are intrinsic to active biological population
  - Relate cell growth and substrate removal to active biomass, which is generally a small fraction of total biomass
- Water9 constants, K_{max} and K_1
  - Relate substrate removal to total biomass population
  - First-order rate constant $K_1 = K_{max}/K_s$, but "effective K_1" determined at typical operating system substrate concentration

40CFR Part63 Appendix C Form XII

1. Add biomass and substrate to serum bottle, aerate.
2. Analyze bottle contents periodically for compound until below detection limit
3. For each time interval between samples, calculate:
   a. removal rate, mg/L-hr
   b. log-mean substrate concentration, S
   c. Ratio of rate to log-mean S
4. Plot reciprocal of ratio vs log-mean S
5. Use slope near Y intercept to determine K_{max} and rate to determine K_1

Using Respirometry Data for Form XII

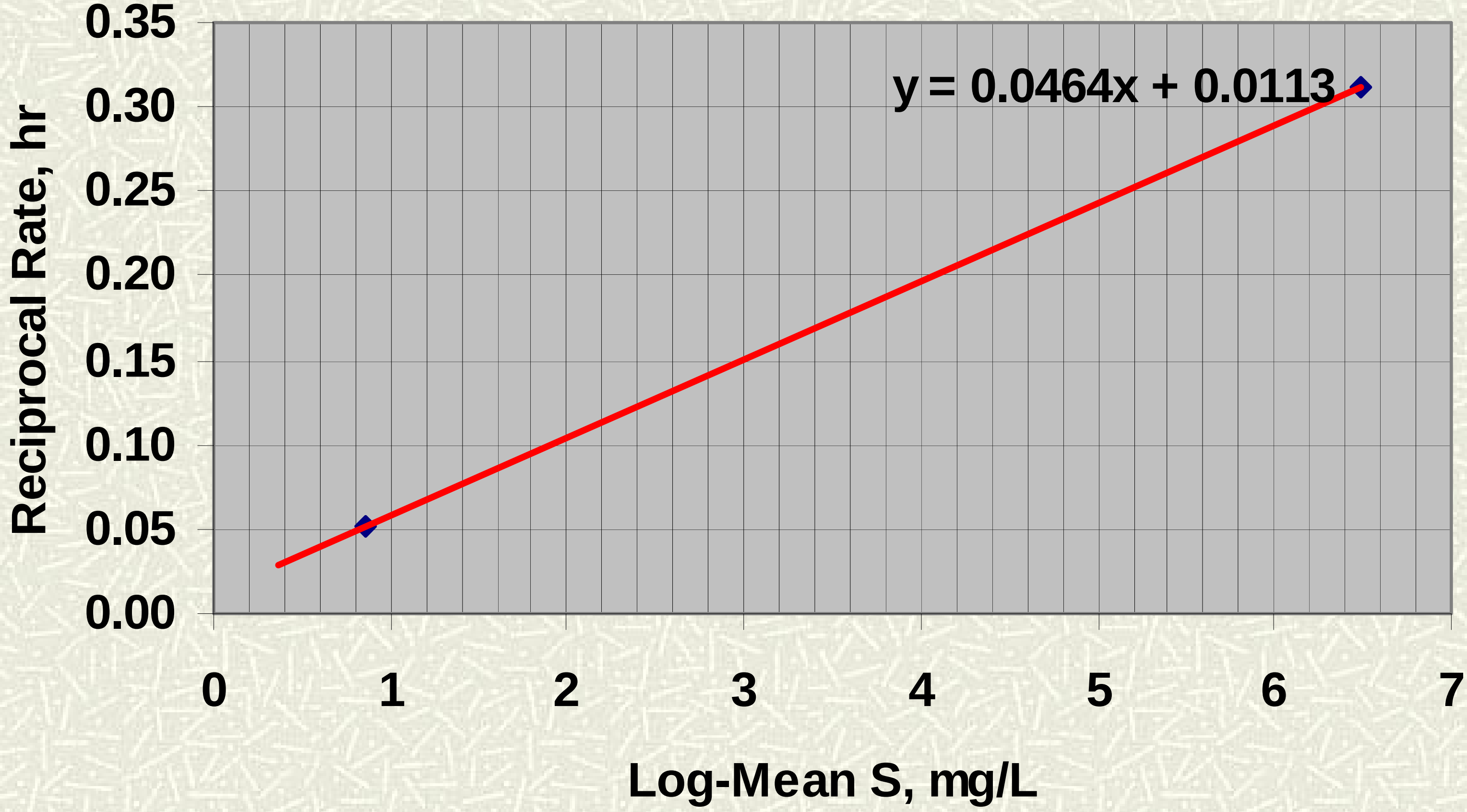
- In place of substrate analyses, use substrate reduction determined from kinetic model fit to respirometry data
  - Select data so that minimum non-zero concentration is close to system operating concentration
- Use Form XII procedure to determine kinetic constants for Water9 model
- Perform analysis on respirometry data from lowest substrate addition, which is closest to plant substrate concentrations

Form XII Data and Calculations

S, mg/L	time, hr	Rate, mg/L-hr	Log-Mean S, mg/L	Ratio Rate/ LM S	Reciprocal Rate, hr
90.60	0				
86.50	6.00	0.6839	88.53	0.0077	129.5
74.59	10.00	2.9774	80.39	0.0370	27.00
34.15	14.00	10.109	51.76	0.1953	5.121
14.78	15.00	19.371	23.13	0.8374	1.194
9.43	15.25	21.402	11.91	1.797	0.556
4.23	15.50	20.788	6.49	3.203	0.312
0.03	15.75	16.808	0.86	19.48	0.051
0.00	16.00	0.130			

Reciprocal Rate vs LM S

Reciprocal Rate vs LM S near Y-Intercept



Determination of K_{max} and K_1 for Water9

$$K_{max} = \frac{1}{\text{slope near intercept} * \text{MLVSS} * \text{HSF}}$$

$$K_1 = \frac{\text{ratio of removal rate to LMS}}{\text{MLVSS} * \text{HSF}}$$

HSF = headspace factor based on Henry's Law Constant and headspace and liquid volumes; ≈ 1.

Form XII Data and Calculations

S, mg/L	time, hr	Rate, mg/L-hr	Log-Mean S, mg/L	Ratio Rate/ LM S hr-1	Reciprocal Rate, hr
90.60	0				
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	19.37	23.13	0.837	[illegible]
[illegible]	[illegible]	21.40	11.91	1.80	0.556
[illegible]	[illegible]	20.79	6.49	3.20	0.312
0.03	15.75	16.81	0.86	19.48	0.051
0.00	16.00	0.130			

Minimum non-zero value should be as close as possible to operating concentration

Slope calculated from orange-highlighted cells

"Effective K_1" calculated from ratio at full system S

Water9 Results for Styrene

	With Water9 Default K's	With K's from Respirometry
K_{max}, hr^{-1}	31.1	7.4
K_1, L/gm-hr	0.11	6.7
Emissions, g/s	0.2	0.007
Effluent, mg/L	1.5	0.006

Caveats

- Calculations based on slope of the asymptote are sensitive to time interval chosen and magnitude of lowest substrate concentration
  - Inherent in the reciprocal rate fitting protocol of Form XII
- Protocol used does not follow the specific Appendix C methodology, and may not be appropriate for regulatory determinations under 40 CFR Part 63 (NESHAPS) without agency approval.

Advantages of Respirometry-based Methodology

- Eliminates:
  - opening of serum bottle for sampling and removal of part of the reactor contents
  - Sampling and analytical uncertainty/variability
- Near-continuous record of O_2 uptake/substrate removal, rather than 6+ discrete points
- Smaller plotting interval for slope near intercept and first-order rate at concentration of concern
- Use of MLVSS at concentration of interest rather than starting concentration.

Summary

- Respirometry can be used to develop kinetic coefficients for use in the Water9 model
- Kinetic coefficients used in Water9 may differ from intrinsic Monod coefficients, despite their similar names and units.

Questions?